Critical Grain Size for Microcracking During Lithium Insertion

Jeff Wolfenstine

ARL-TN-129   December 1998

Army Research Laboratory

Adelphi, MD 20783-1197

ARL-TN-129   **December 1998**

Critical Grain Size for Microcracking During Lithium Insertion

Jeff Wolfenstine
Sensors and Electron Devices Directorate

Abstract

I derived a critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or grain size is not a practical solution for solving the mechanical instability problem of Li-alloys.

Contents

1. Introduction

The use of Li-alloys (e.g., Li_xM, where M = Al, Bi, Sn, Si, and Ga) as anodes in Li batteries leads to improved safety and faster cycling rates compared to pure Li [1–5]. A disadvantage of Li-alloys compared to pure Li as anodes is a reduction in specific energy and energy density. Another problem with Li-alloy electrodes is mechanical instability. Mechanical instability refers to the microcracking/crumbling of the alloy when Li is inserted/removed during charging/discharging. Some potential solutions to solve the mechanical instability problem include [6–9] (i) incorporating the alloys within a ductile Li-ion conducting metal or polymer matrix or (ii) decreasing the alloy particle and/or grain size. A decrease in the particle and/or grain size is also important from an electrochemical viewpoint, as it can lead to faster cycling rates [10]. However, many questions remain, and among them are these two: How small a grain size is required for the Li-alloys to exhibit mechanical stability during lithium charging/discharging? Are grain sizes of Li-alloy particles produced using new nanophase (particle sizes between 10 to 100 nm) techniques small enough?

This technical note attempts to answer the above questions by determining a critical grain size below which microcracking and, hence, disintegration of the Li-alloy anodes does not occur during Li charging.

2. Discussion

Microcracking occurs in Li-alloys as a result of volume expansion during Li charging. The determination of the critical grain size below which microcracking does not occur is based on an energy criterion. The basic concept of the energy criterion is that the strain energy (generated due to a volume difference between phases) released when microcracks form must equal or exceed that required for the creation of new fracture surfaces. The energy criterion has been successfully applied to explain crack formation in brittle materials, microcracking due to thermal shock, and thermal expansion anisotropy [11–13].

We can start with a single particle composed of fine equiaxed grains. The total energy of this system, U_{tot}, is given as follows [11–13]:

$$U_{tot} = U_0 - U_{strain} + U_{surface} , \qquad (1)$$

where U_0 is the energy of the unmicrocracked particle, U_{strain} is the strain energy per unit volume, and $U_{surface}$ is the surface energy per unit area. The following discussion assumes that microcracking (i) is due to tensile stresses generated as a result of volume expansion and (ii) occurs along grain boundaries. Assuming a dodecahedral grain morphology of grain size, d, equation (1) reduces to [13]

$$U_{tot} = U_0 - 7.66 \, NU_{strain} \, d^3 + 20.65 \, N\gamma d^2 , \qquad (2)$$

1

where N is the number of grains that relieve their elastic strain energy by microcracking and γ is the surface energy. The critical grain size, d_{crit}, is calculated by differentiating equation (2) and equating it to zero as follows:

$$d_{crit} = 1.79 \ \gamma/U_{strain} \ . \tag{3}$$

The importance of equation (3) is that a material with a grain size smaller than d_{crit} will not exhibit microcracking; whereas if the grain size is greater than d_{crit}, it will exhibit microcracking. Assuming only elastic behavior, the strain energy is given as follows:

$$U_{strain} = \sigma^2/2E \ , \tag{4}$$

where σ is the stress and E is the elastic modulus. For the case of a volume change, the stress is given as follows [14]:

$$\sigma = \frac{E}{3(1-2v)} \frac{\Delta V}{V_0} \ , \tag{5}$$

where ΔV is the volume change, V_0 is the initial volume, and v is Poisson's ratio. Substituting equation (5) into equation (4) and combining it with equation (3) yields the following equation for the critical grain size as a function of volume change:

$$d_{crit} = \frac{32.2\gamma(1-2v)^2 V_0^2}{E\Delta V^2} \ . \tag{6}$$

Equation (6) can be used to determine how small a grain size is required for Li-alloys (e.g., Li_xM, where M = Al, Bi, Sn, Si, and Ga) that are used as anodes and that do not exhibit microcracking during lithium charging. A material with a grain size less than d_{crit} (eq. (6)) will not exhibit microcracking as a result of tensile stresses generated due to a volume expansion.

What is the critical grain size of an Li-alloy that is to be used as an anode in Li batteries? For example, take $Li_{4.4}Sn$. This binary alloy has the highest Li capacity in the Li-Sn system [7]. The volume change, $\Delta V/V_0$, from Sn to $Li_{4.4}Sn$ is 2.59 per atom of Sn [7,15]. Determination of the critical grain size also requires that E, v, and γ be known. Unfortunately, a review of the literature did not reveal the values of E, v, and γ for $Li_{4.4}Sn$. The average E for 20 other intermetallic alloys is close to 200 GPa [16]. The surface energy for brittle materials is typically between 0.3 to 1.2 J/m^2 [17]. Using E = 200 GPa, γ = 0.75 J/m^2, v = 0.33 (a typical value for a crystalline solid), and $\Delta V/V_0$ = 2.59, the critical grain size below which microcracking will not occur during Li charging of Sn to $Li_{4.4}Sn$ can be determined. Inserting these values into equation (6) yields a predicted $d_{crit} \approx 0.002$ nm. If the value of the surface energy is off by a factor of 2, and the elastic modulus is off by a factor of 10, the predicted critical grain size is still less than 0.040 nm. It is important to note that this grain size (0.040 nm) is about 12 to 13 times smaller than the size of an Sn unit cell (≈ 0.5 nm). A similar

2

calculation for $Li_{4.4}Si$ ($\Delta V/V_0$ = 3.12 [7]) yields a predicted $d_{crit} \approx$ 0.0014 nm. These results suggest that it is almost impossible to obtain a fine enough grain size to prevent microcracking during Li charging of a single-phase material. It is believed that this is primarily a result of the strain energy generated by large tensile stresses due to the volume change that cannot be accommodated by plastic deformation due to the brittle nature (significant fraction of covalent or ionic bonding) of the material and, hence, microcracking occurs. The above predictions are in agreement with experimental electrochemical results, which reveal that it is almost impossible to electrochemically insert Li into fine grain pure metals such as Sn to form Li-Sn alloys without the alloys suffering cracking/disintegration [15,18]. Even if a sacrifice in capacity is made to reduce the amount of volume expansion, the predicted critical grain size is still less than the size of a unit cell for most of the Li-alloys. For example, Li charging of Sn to form LiSn ($\Delta V/V_0$ = 0.53) instead of $Li_{4.4}Sn$ only increases the critical grain size by a factor of about 25, to about 0.05 nm. This grain size is still much smaller than the size of the Sn unit cell. The above predictions and their agreement with the experimental observations emphasize that producing a fine enough grain size in an intrinsically brittle single-phase material to prevent microcracking as a result of a volume expansion due to Li charging is highly unlikely, no matter what processing technique is used, including new nanophase techniques.

The results suggest that decreasing the particle and the grain size is not a practical solution to solve the mechanical instability problem of Li-alloys. More likely solutions to solve this problem include (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix as previously suggested [6–9] or (ii) surrounding the alloys within a matrix that places them under compressive stresses to prevent microcracking formation. This suggestion may explain why SnO and SnO_2 can be cycled, whereas metallic Sn cannot [15,18,19]. It has been observed that as Li is initially titrated into SnO or SnO_2, it decomposes to Li_2O and Sn. Upon further Li addition, a series of Li-Sn alloys form with increasing Li content until a final alloy composition of $Li_{4.4}Sn$ is reached [15,19,20]. It is likely that the Li_2O surrounding the Li-Sn alloys supplies a residual compressive stress that prevents the Li-Sn alloys from suffering mechanical deterioration during repeated charging/discharging. This same reasoning may also explain why $Li_2MnO_4/Na_{0.7}MnO_2$ composites exhibit better capacity retention during cycling in the 3-V region compared to single-phase Li_2MnO_4 [21].

3. Conclusions

A critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys was derived based on energy considerations. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or the grain size is not a practical solution for solving the mechanical instability problem associated

with Li-alloys. More likely solutions to this problem include (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix or (ii) surrounding the alloys within a matrix that places them under a compressive stress.

Acknowledgments

References

[1] K. M. Abraham, *Electrochimica Acta*, **38** (1993), 1233.

[2] Z. Takehara and K. Kanamura, *Electrochimica Acta*, **38** (1993), 1169.

[3] R. A. Huggins, *J. Power Sources*, **22** (1988), 341.

[4] R. A. Huggins, *J. Power Sources*, **26** (1989), 109.

[5] A. Anani, S. Crouch-Baker, and R. A. Huggins, *J. Electrochem. Soc.*, **134** (1987), 3098.

[6] M. Maxfield, T. R. Jow, S. Gould, M. G. Sewchok, and L. W. Shacklette, *J. Electrochem. Soc.*, **135** (1988), 299.

[7] B. A. Boukamp, G. C. Lesh, and R. A. Huggins, *J. Electrochem. Soc.*, **128** (1981), 725.

[8] J. O. Besenhard, J. Yang, and M. Winter, *J. Power Sources*, **68** (1997), 109.

[9] J. Yang, M. Winter, and J. O. Besenhard, *Solid State Ionics*, **90** (1996), 281.

[10] K. M. Abraham, D. M Pasquareillo, and E. M. Willstaedt, *J. Electrochem. Soc.*, **145** (1998), 482.

[11] D. P. H. Hasselman, *J. Amer. Ceram. Soc.*, **46** (1963), 535.

[12] J. P. A. Tillet, *Proc. Phys. Soc. London, Ser. B*, **69** (1956), 47.

[13] J. J. Cleveland and R. C. Bradt, *J. Amer. Ceram. Soc.*, **61** (1978), 478.

[14] M. W. Barsum, *Fundamentals of Ceramics*, McGraw-Hill, New York (1997), p 502.

[15] I. A. Courtney and J. R. Dahn, *J. Electrochem. Soc.*, **144** (1997), 2045.

[16] K. Tanaka and M. Kiowa, *Intermetallics*, **4** (1996), S29.

[17] I. LeMay, *Principles of Mechanical Metallurgy*, Elsevier, New York (1981), p 218.

[18] T. Brousse, R. Retoux, U. Herterich, and D. M. Schleich, *J. Electrochem. Soc.*, **145** (1998), 1.

[19] C.-K. Huang, J. S. Sakamoto, M. C. Smart, S. Surampudi, and J. Wolfenstine, *Materials for Electrochemical Energy Storage and Conversion II-Batteries, Capacitors and Fuel Cells*, D. S. Ginley, D. H. Doughty, T. Takamura, Z. Zhang, and B. Scrosati, eds., **496**, Materials Research Society, Warrendale, PA (1998), p 519.

[20] J. Wolfenstine, J. Sakamoto, and C.-K. Huang, *J. Power Sources*, **75** (1998), 181.

[21] J. Kim and A. Manthiram, *Electrochemical and Solid-State Letters*, **1** (1998), 201.

Distribution

Admnstr
Defns Techl Info Ctr
Attn DTIC-OCP
8725 John J Kingman Rd Ste 0944
FT Belvoir VA 22060-6218

Ofc of the Dir Rsrch and Engrg
Attn R Menz
Pentagon Rm 3E1089
Washington DC 20301-3080

Ofc of the Secy of Defns
Attn ODDRE (R&AT)
Attn ODDRE (R&AT) S Gontarek
The Pentagon
Washington DC 20301-3080

OSD
Attn OUSD(A&T)/ODDDR&E(R) R J Trew
Washington DC 20301-7100

Advry Grp on Elect Devices
Attn Documents
Crystal Sq 4 1745 Jefferson Davis Hwy Ste 500
Arlington VA 22202

AMCOM MRDEC
Attn AMSMI-RD W C McCorkle
Redstone Arsenal AL 35898-5240

CECOM Night Vsn/Elect Sensors Dirctrt
Attn AMSEL-RD-NV-D
FT Belvoir VA 22060-5806

Commander
CECOM R&D
Attn AMSEL-IM-BM-I-L-R Stinfo Ofc
Attn AMSEL-IM-BM-I-L-R Techl Lib
FT Monmouth NJ 07703-5703

Deputy for Sci & Techlgy
Attn Ofc Asst Sec Army (R&D)
Washington DC 30210

Dir ARL Battlefield Envir Dirctrt
Attn AMSRL-BE
White Sands Missile Range NM 88002-5501

Dir for MANPRINT
Ofc of the Deputy Chief of Staff for Prsnnl
Attn J Hiller
The Pentagon Rm 2C733
Washington DC 20301-0300

Hdqtrs
Attn DAMA-ARZ-D F D Verderame
Washington DC 20310

Hdqtrs Dept of the Army
Attn DAMO-FDT D Schmidt
400 Army Pentagon Rm 3C514
Washington DC 20301-0460

US Army Armament Rsrch Dev & Engrg Ctr
Attn AMSTA-AR-TD M Fisette
Bldg 1
Picatinny Arsenal NJ 07806-5000

Commander
US Army CECOM
Attn AMSEL-RD-CZ-PS-B M Brundage
FT Monmouth NJ 07703-5000

US Army CECOM Rsrch Dev & Engrg Ctr
Attn AMSEL-RD-AS-BE E Plichta
FT Monmouth NJ 07703-5601

US Army Edgewood RDEC
Attn SCBRD-TD G Resnick
Aberdeen Proving Ground MD 21010-5423

US Army Info Sys Engrg Cmnd
Attn ASQB-OTD F Jenia
FT Huachuca AZ 85613-5300

US Army Natick RDEC
Acting Techl Dir
Attn SSCNC-T P Brandler
Natick MA 01760-5002

Director
US Army Rsrch Ofc
4300 S Miami Blvd
Research Triangle Park NC 27709

Distribution (cont'd)

US Army Rsrch Ofc
Attn AMXRO-ICA B Mann
PO Box 12211
Research Triangle Park NC 27709-2211

US Army Simulation, Train, & Instrmntn
    Cmnd
Attn J Stahl
12350 Research Parkway
Orlando FL 32826-3726

US Army Tank-Automtv Cmnd Rsrch, Dev, &
    Engrg Ctr
Attn AMSTA-TA J Chapin
Warren MI 48397-5000

US Army Train & Doctrine Cmnd
Battle Lab Integration & Techl Dirctrt
Attn ATCD-B J A Klevecz
FT Monroe VA 23651-5850

US Military Academy
Mathematical Sci Ctr of Excellence
Attn MDN-A MAJ M D Phillips
Dept of Mathematical Sci Thayer Hall
West Point NY 10996-1786

Nav Rsrch lab
Attn Code 2627
Washington DC 20375-5000

Nav Surface Warfare Ctr
Attn Code B07 J Pennella
17320 Dahlgren Rd Bldg 1470 Rm 1101
Dahlgren VA 22448-5100

Marine Corps Liaison Ofc
Attn AMSEL-LN-MC
FT Monmouth NJ 07703-5033

USAF Rome Lab Tech
Attn Corridor W Ste 262 RL SUL
26 Electr Pkwy Bldg 106
Griffiss AFB NY 13441-4514

DARPA
Attn B Kaspar
3701 N Fairfax Dr
Arlington VA 22203-1714

Hicks & Associates, Inc
Attn G Singley III
1710 Goodrich Dr Ste 1300
McLean VA 22102

Palisades Inst for Rsrch Svc Inc
Attn E Carr
1745 Jefferson Davis Hwy Ste 500
Arlington VA 22202-3402

Dir ARL Sensors, Signatures, Signal & Info
    prcsg Dirctrt (S3I)
Attn AMSRL-SS
Adelphi MD 20783-1197

US Army Rsrch Lab
Attn AMSRL-D R W Whalin
Attn AMSRL-DD J Rocchio
Attn AMSRL-DD COL T A Dunn
Attn AMSRL-CI-LL Techl Lib (3 copies)
Attn AMSRL-CS-AS Mail & Records Mgmt
Attn AMSRL-CS-EA-TP Techl Pub (3 copies)
Attn AMSRL-DC S Gilman
Attn AMSRL-DC T Wolfenstine (25 copies)
Attn AMSRL-SE J Mait
Attn AMSRL-SE-D E Scannell
Adelphi MD 20783-1197

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE December 1998	3. REPORT TYPE AND DATES COVERED Final, Oct 15–Nov 5 1998

4. TITLE AND SUBTITLE Critical Grain Size for Microcracking During Lithium Insertion

6. AUTHOR(S) Jeff Wolfenstine

5. FUNDING NUMBERS

DA PR: AH47

PE: 61102A

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
Attn: AMSRL-SE-DC   email: jef_wolfenstine@stinger.arl.mil
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TN-129

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
2800 Powder Mill Rd
Adelphi, MD 20783-1197

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
ARL PR: 9NENV2
AMS code: 611102.H47

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

I derived a critical grain size below which microcracking does not occur based on volume changes as a result of Li charging into brittle Li-alloys. The predicted critical grain size is less than the unit cell size for a majority of single-phase materials. This suggests that decreasing the particle and/or grain size is not a practical solution for solving the mechanical instability problem of Li-alloys.

14. SUBJECT TERMS
Li-ion batteries, brittle fracture, mechanical instability, Li-alloys, anodes, charging

15. NUMBER OF PAGES
14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102